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A consistent interpretation of the magneto-optical spectra of spinel type ferrites (invited)

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Through a systematic investigation of the complete dielectric tensor, between 0.5 and 5.0 eV, of Fe_3O_4 and of related spinel ferrites, i.e., MgFe_2O_4 , $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$, NiFe_2O_4 , and CoFe_2O_4 , we have established that intervalence charge transfer and intersublattice charge transfer transitions dominate the optical and magneto-optical spectrum (between 0.5 and 5.0 eV) of all spinel ferrites of the general composition $\text{Me}_x\text{Fe}_{3-x}\text{O}_4$. In all cases examined the same set of intersublattice charge transfer transitions was observed. These are the only transitions observed in the cases where Me is a nonmagnetic ion (Mg^{2+} , Li^+). In the cases where Me is a magnetic ion (Fe^{2+} , Ni^{2+} , Co^{2+}) additional intervalence charge transfer transitions are observed. CoFe_2O_4 is the only spinel ferrite with a major contribution of crystal field transitions to the magneto-optical spectrum. The observed presence of only two intense crystal field transitions in specifically CoFe_2O_4 is explained. The observed relative strengths of these two transitions in CoFe_2O_4 , in which remarkably the upper transition at 1.82 eV is more intense than the lower transition at 0.83 eV is also explained in a crystal field analysis. © 1999 American Institute of Physics. [S0021-8979(99)42508-3]

I. INTRODUCTION

Spinel type ferrites are compounds with the cubic spinel type structure and the general formula $\text{Me}_x\text{Fe}_{3-x}^{3+}\text{O}_4$. In most important magnetic ferrites Me is a divalent metal cation. In a "normal" spinel ferrite the divalent Me ions are located on the tetrahedral sites. Fe_3O_4 , or magnetite, crystallizes in the inverse spinel structure, with cation distribution $(\text{Fe}^{3+})[\text{Fe}^{3+}\text{Fe}^{2+}]\text{O}_4$. In this structural formula the parentheses denote tetrahedral sites and the square brackets denote the octahedral sites. Most of the properties of ferrites have been thoroughly studied and are well documented.^{1,2} However, the electronic structure of Fe_3O_4 and that of related compounds is still a subject of debate. The rather complex electronic structure of transition metal oxides in general has led for Fe_3O_4 and related ferrites to a confusing variety of interpretations of the optical and magneto optical (MO) Kerr spectra, due to different assignments of the observed transitions.³⁻⁶

Recently, we measured both the optical and MO polar Kerr spectra of pure Fe_3O_4 and of Mg^{2+} - and Al^{3+} -substituted Fe_3O_4 and from these the complete dielectric tensors of these compounds between 0.7 and 4.0 eV were determined.⁷ Subsequently, the MO spectrum of Fe_3O_4 between 0.7 and 4.0 eV was resolved through fitting simultaneously both the diagonal and the off-diagonal elements of this tensor with a single set of transitions and this consistently for all partially substituted ferrite samples. This en-

abled the assignment of all major transitions in Fe_3O_4 to intervalence and intersublattice charge transfer [(IVCT) and (ISCT), respectively] transitions.

Essentially the same method was used to reexamine the MO spectra of $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$, MgFe_2O_4 , NiFe_2O_4 , and CoFe_2O_4 between 0.5 and 5.0 eV from literature data.⁸ This analysis revealed that the common feature of all spinel ferrites of the general type $\text{Me}_x\text{Fe}_{3-x}\text{O}_4$ with Fe^{3+} ions on both tetrahedral and octahedral sites, is a set of ISCT transitions between 2.5 and 4.0 eV. These transitions dominate the spectrum for those spinel ferrites where Me is a nonmagnetic ion, for instance, Mg^{2+} or Li^+ . In Fe_3O_4 several IVCT transitions between $[\text{Fe}^{2+}]$ and Fe^{3+} are main contributors. In NiFe_2O_4 an IVCT between $[\text{Ni}^{2+}]$ and $[\text{Fe}^{3+}]$ is a main contributor. In CoFe_2O_4 crystal field (CF) transitions of tetrahedrally coordinated Co^{2+} and an IVCT transition between $[\text{Co}^{2+}]$ and $[\text{Fe}^{3+}]$ contribute significantly below 2.5 eV.

II. THEORY

A. Intervalence charge transfer transitions

IVCT transitions are transitions in which an electron, through optical excitation, is transferred from one cation to a neighboring cation. Compounds containing an element in two different oxidation states, mixed valence compounds, often show intense absorption in the visible region which can be attributed to IVCT transitions. Examples include halides [for instance $\text{Pd}(\text{NH}_3)_2\text{Cl}_3$], cyanides [for instance $\text{KFe}_2(\text{CN})_6$] and oxides (for instance Pb_3O_4).⁹ Another example of such a compound is Fe_3O_4 , which contains Fe^{2+}

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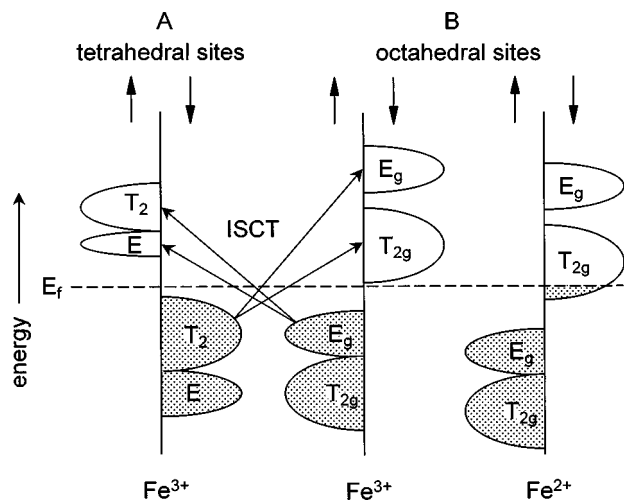


FIG. 1. Schematic representation of the electron energy levels of the Fe ions in Fe_3O_4 , including the relevant ISCT transitions.

and Fe^{3+} . In this case, the IVCT bands can be considered as the result of electronic transitions between weak Fe–Fe bonding and antibonding orbitals which are a result of overlapping Fe($3d$) orbitals, across the shared edges of adjacent Fe–O polyhedra. In Fe_3O_4 the electron transfer between Fe^{2+} and Fe^{3+} may be mediated by O^{2-} ions, in particular when e_g orbitals are involved. In such a case, the transfer occurs more readily for smaller electrostatic polarization of the O^{2-} ions.^{9,10} Between Fe t_{2g} orbitals direct electron transfer is possible as a result of the overlap between these orbitals. The key distinction between IVCT transitions and CF transitions is that the former involves two cations while the latter is a single-ion transition. As a result, the parity selection rule is relaxed for IVCT transitions.¹¹ Note that IVCT transitions between Fe^{3+} ions on different crystallographic sites, as depicted in Fig. 1, are traditionally called ISCT transitions.¹¹ For reasons of clarity we will continue to refer to these transitions as ISCT transitions.

The role of the lattice in IVCT transitions may be discussed qualitatively with a configuration coordinate diagram as presented in Fig. 2 where each of the two paraboles corresponds to the electron being situated at a distinct site.⁶ For two equivalent sites Fig. 2(a) applies, the dotted line representing the potential energy in case of a partly delocalized electron. As illustrated by the arrow, upon absorption of a photon with an energy equal to E_{op} the electron is transferred from one site to another. The transfer occurs on an electronic timescale which the lattice cannot follow due to the large ionic mass(es). As a result, the lattice coordinate, Q , does not change during the transition (Franck–Condon principle). Indicated in this figure is also the activation energy for thermal charge transfer, E_{th} . The case of two nonequivalent sites is depicted in Fig. 2(b). As this figure indicates, optical IVCT transitions between cations on nonequivalent sites occur at higher energies than comparable IVCT transitions between cations on equivalent sites. Furthermore, the thermal activation energy is larger which may lead to localization of the electron in absence of optical excitation. Finally, if the electron is optically transferred to a neighboring nonequivalent

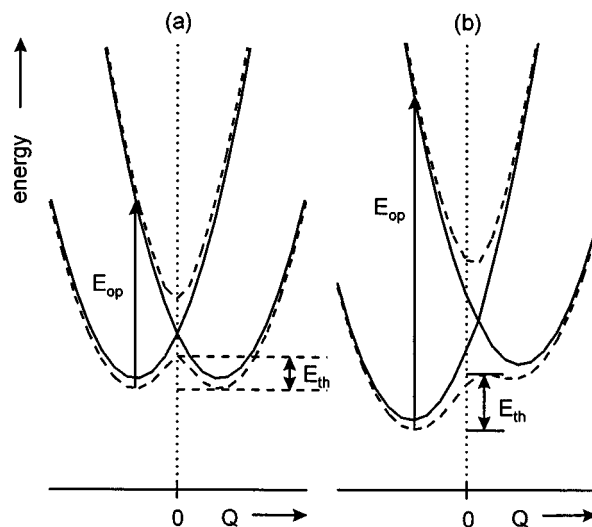


FIG. 2. Simplified diagrams of potential energy versus configuration coordinate for two equivalent sites (a) and for two nonequivalent sites (b).

cation site, a metastable situation results. The lifetime of this, in essence, excited state will be short, as the activation energy for the electron to revert to the ground state through thermal charge transfer is small.^{6,10}

B. Crystal-field transitions

To examine which $3d$ crystal-field (CF) transitions are possible in spinel ferrites, we first discuss Fe_3O_4 . CF transitions of ions on octahedral sites are parity forbidden for any ion due to the inversion symmetry. In addition CF transitions involving Fe^{3+} are also spin forbidden. CF transitions of Fe^{3+} on the A sites are slightly parity allowed due to the lack of inversion symmetry in the crystal field at that site. However, CF transitions of Fe^{3+} on tetrahedral sites do not occur at optical frequencies, as the term of a free Fe^{3+} ion is non-degenerate ($L=0$). CF transitions of Me^{2+} on A sites are spin allowed and slightly parity allowed, however, the Fe^{2+} cations in Fe_3O_4 have a strong octahedral site preference.¹ As a result, in Fe_3O_4 , CF transitions have a low oscillator strength. In mixed ferrites, however, the inversion symmetry on B sites can be lost due to distortion of the octahedral symmetry, which may lead to stronger CF transitions. Furthermore, in ferrites with ions in the high spin state on A sites, for instance Co^{2+} ions in cobalt ferrite, CF transitions of considerable strength may be observed.

The electronic structure of the Co^{2+} ion (d^7) in tetrahedral coordination is equivalent to that of d^3 in octahedral coordination. According to standard crystal-field theory¹² the ground state is a 4A_2 state, while the excited states are a 4T_2 and two 4T_1 states, of which the lowest is derived mainly from 4F , the highest mainly from 4P . The only allowed optical transitions are from the 4A_2 ground state to the two 4T_1 states. The splitting as well as the intensity ratio of these two lines are most conveniently obtained in the strong-field scheme, where the configuration of the ground state is t_2^3 and the 4T_1 states are $|{}^4T_1(t_2^2e)\rangle = (|{}^4F\rangle + 2|{}^4P\rangle)/\sqrt{5}$ and $|{}^4T_1(t_2e^2)\rangle = (-2|{}^4F\rangle + |{}^4P\rangle)/\sqrt{5}$. One finds $h\nu_{\pm} = (15B + 3\Delta \pm R)/2$ and

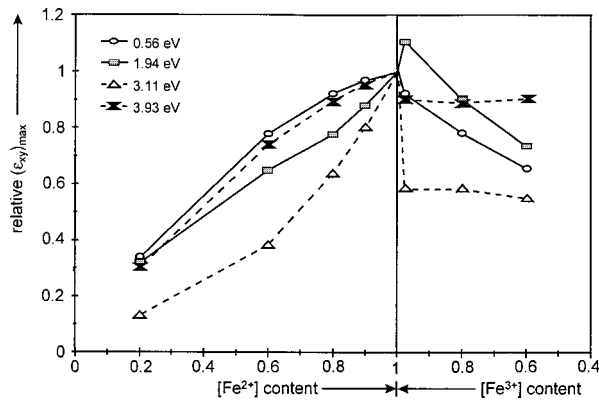


FIG. 3. Relative maximum ϵ_{xy} value for the IVCT transitions; vs $[\text{Fe}^{2+}]$ content (Mg^{2+} substitution) and vs $[\text{Fe}^{3+}]$ content (Al^{3+} substitution).

$$|^4T_1(-)\rangle = -\sin \alpha |^4T_1(t_2^2e)\rangle + \cos \alpha |^4T_1(t_2e^2)\rangle, \quad (1)$$

$$|^4T_1(+)\rangle = \cos \alpha |^4T_1(t_2^2e)\rangle + \sin \alpha |^4T_1(t_2e^2)\rangle, \quad (2)$$

with $R = \sqrt{(9B - \Delta)^2 + 144B^2}$ and $\tan 2\alpha = 12B/(9B - \Delta)$, where B is the Co^{2+} Racah parameter and Δ is the crystal field splitting between t_2 and e orbitals. Thus the mean frequency and the splitting of the lines are $\hbar\bar{\omega} = 15B + 3\Delta$ and $|h\omega_+ - h\omega_-| = R$. Since in an ordinary dipole transition only a single electron can be promoted to an excited orbital, the

only nonzero dipole matrix element is that between $^4A_2(t_2^3)$ and $^4T_1(t_2^2e)$. Therefore the intensity ratio, I , of the lines is given by

$$I = \frac{I[^4A_2 \rightarrow ^4T_1(-)]}{I[^4A_2 \rightarrow ^4T_1(+)]} = \frac{\omega_-}{\omega_+} \tan^2 \alpha. \quad (3)$$

It follows that the maximum value I can reach is $5/9$ (when $\alpha = \pi/4$).

In conclusion, the only two MO active CF transitions which are allowed for the spinel ferrites considered here are $^4A_2 \rightarrow ^4T_1(F)$ and $^4A_2 \rightarrow ^4T_1(P)$ of tetrahedrally coordinated ions in the spin state, i.e., Co^{2+} on A sites.

III. RESULTS AND DISCUSSION

A. Fe_3O_4

We unraveled the MO Kerr spectrum of Fe_3O_4 between 0.7 and 4.0 eV by applying a rigorous fitting procedure in which all four elements of the dielectric tensor of Fe_3O_4 were fitted *simultaneously*, using the equations of the elements of the dielectric tensor which describe the basic line shapes of transitions in the microscopic theory. In addition, the complete dielectric tensors of Fe_3O_4 and of partially Mg^{2+} or Al^{3+} substituted Fe_3O_4 were fitted *consistently* with a single set of transitions for all samples.⁷ As shown in Fig. 3, the relative intensity of certain MO transitions

TABLE I. The main MO-active transitions in Fe_3O_4 , MgFe_2O_4 , $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$, CoFe_2O_4 , and NiFe_2O_4 between 0.5 and 5.0 eV. Listed are transition energy ω [eV], linewidth Γ [eV], intensity $(\epsilon_{xy})_{\text{max}}$, and assignment. Typical errors for ω , Γ , and $(\epsilon_{xy})_{\text{max}}$ are ± 0.02 , ± 0.03 , and ± 0.002 eV, respectively. (Note that the parentheses denote tetrahedral coordination and square brackets octahedral coordination.)

Sample	Assignment	IVCT	IVCT	IVCT	IVCT	ISCT	ISCT	ISCT
		$[\text{Fe}^{2+}]t_{2g}$	$[\text{Fe}^{2+}]t_{2g}$	$[\text{Fe}^{2+}]t_{2g}$	$[\text{Fe}^{2+}]t_{2g}$	$(\text{Fe}^{3+})t_2$	$[\text{Fe}^{3+}]e_g$	$(\text{Fe}^{3+})t_2$
		\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow
		$[\text{Fe}^{2+}]t_{2g}$	$[\text{Fe}^{2+}]e_g$	$(\text{Fe}^{2+})e$	$(\text{Fe}^{2+})t_2$	$[\text{Fe}^{2+}]t_{2g}$	$(\text{Fe}^{2+})t_2$	$[\text{Fe}^{2+}]e_g$
Fe_3O_4	ω	0.56	1.94	3.11	3.93	2.61	3.46	3.94
	Γ	0.21	0.45	0.61	0.37	0.20	0.42	0.51
	$(\epsilon_{xy})_{\text{max}}$	-0.085	0.044	0.031	-0.039	-0.004	0.014	0.065
	shape	para	para	dia	dia	dia	dia	dia
MgFe_2O_4	ω					2.64	3.47	3.95
	Γ					0.30	0.31	0.56
	$(\epsilon_{xy})_{\text{max}}$					-0.009	0.022	0.032
	shape					dia	dia	dia
$\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$	ω					2.63	3.46	4.09
	Γ					0.23	0.39	0.64
	$(\epsilon_{xy})_{\text{max}}$					-0.026	0.036	0.050
	shape					dia	dia	dia
		CF	CF	IVCT				
		(Co^{2+})	(Co^{2+})	$[\text{M}^{2+}]$				
		$^4A_2 \rightarrow$	$^4A_2 \rightarrow$	\rightarrow				
		$^4T_1(F)$	$^4T_1(P)$	$[\text{Fe}^{2+}]t_{2g}$				
CoFe_2O_4	ω	0.83	1.82	2.21	± 2.60	3.55	4.00	
	Γ	0.10	0.18	0.25		0.29	0.50	
	$(\epsilon_{xy})_{\text{max}}$	-0.056	-0.076	-0.054	<0.001	0.013	0.030	
	shape	dia	para	para	dia	dia	dia	
NiFe_2O_4	ω			2.86	2.57	3.46	4.03	
	Γ			0.53	0.22	0.54	0.67	
	$(\epsilon_{xy})_{\text{max}}$			0.023	-0.007	0.011	0.017	
	shape			dia	dia	dia	dia	

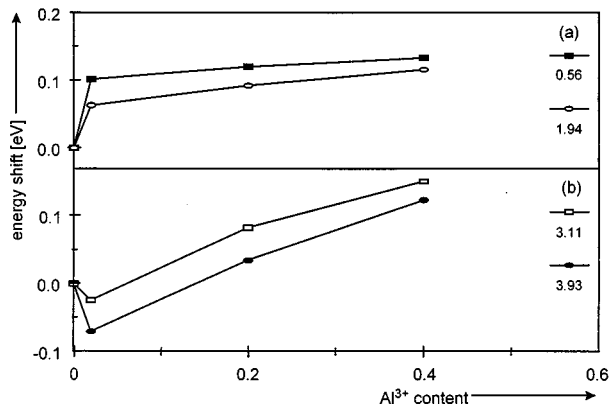


FIG. 4. Change in energy upon Al^{3+} substitution for the IVCT transitions in Fe_3O_4 at 0.56 and 1.94 eV (a) and at 3.11 and 3.93 eV (b).

depends on both $[\text{Mg}^{2+}]$ (which substitutes $[\text{Fe}^{2+}]$) and on $[\text{Al}^{3+}]$ (which substitutes $[\text{Fe}^{3+}]$). These transitions can therefore be identified unambiguously as IVCT transitions. As a consequence, all the major transitions in the Fe_3O_4 MO Kerr spectrum could be assigned to IVCT and ISCT transitions based on the energy level scheme depicted in Fig. 1. The transitions identified are given in Table I.

The shifts in transition energy upon substitution further confirm these assignments. The lattice parameter of $\text{Al}_x\text{Fe}_{3-x}\text{O}_4$ decreases linearly with x ,^{13,14} the decrease being due to the small ion radius of $[\text{Al}^{3+}]$ relative to $[\text{Fe}^{3+}]$. Furthermore, the energy of an IVCT transition changes with the internuclear distance of the participating cations as Fig. 2 indicates. In Fig. 4 the change in energy of the IVCT transitions at 0.56 and 1.94 eV (a) and at 3.11 and 3.93 eV (b) as a function of Al^{3+} content is shown. We observe, first, that the changes in energy are proportional to the Al^{3+} content, after an initial jump which we have related previously to the perturbation of the octahedral symmetry,⁷ and second, that the magnitude of the energy shift differs remarkably for the two sets of transitions. As shown in Table I, the transitions at 0.56 and 1.94 eV are of the octahedron-octahedron type with a direct overlap of the orbitals involved. In contrast, the transitions at 3.11 and 3.93 eV are of the octahedron-tetrahedron type for which the charge transfer between the orbitals involved is mediated by O^{2-} . From the spinel-type structure one infers that replacing one of the octahedrally coordinated iron ions will influence the relative positions of the surrounding oxygen ions more than the positions of the remaining octahedral cations relative to each other. As a consequence, ISCT transitions would be more sensitive to Al^{3+} substitution and the observed difference in energy shift is consistent with the above assignment. The increase in the electrostatic polarization of the O^{2-} ion as a result of the small Al^{3+} ion radius may be an alternative explanation for the observed difference. The shifts in energy upon Mg^{2+} substitution are relatively small (< 0.05 eV) for all IVCT transitions. In this case no linear dependence was observed, probably due to slight variations in the cation distribution.

B. MgFe_2O_4 , $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$, and NiFe_2O_4

As seen in Table I, the three ISCT transitions are the only major transitions in MgFe_2O_4 . This is to be expected, since the Fe^{2+} ions responsible in Fe_3O_4 for the intense IVCT transitions are replaced by the nonmagnetic Mg^{2+} .⁸ In Fig. 5 the fit of the real and imaginary parts of the off-diagonal element of the dielectric tensor, ϵ'_{xy} and ϵ''_{xy} of $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ is presented. In $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ the same three ISCT transitions are identified. The fact that the intensities are in this case substantially higher is to be expected as this compound contains a larger amount of $[\text{Fe}^{3+}]$, which is one of the participating ions in the transitions.^{8,15} We also observe several weak and narrow additional transitions. These are most likely CF transitions of $[\text{Fe}^{3+}]$ for which the parity selection rule is relaxed, since in $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ the inversion symmetry of octahedral sites is lost. Note, that these CF transitions are still spin forbidden which can account for the fact that these transitions are significantly less intense (by a factor 10 to 20) than the allowed CF transitions in CoFe_2O_4 (see Sec. III C). The same set of ISCT transitions is also observed in yttrium-iron-garnet (YIG)¹¹ and dominates the spectrum of $\gamma\text{-Fe}_2\text{O}_3$ which has the same shape as that of MgFe_2O_4 . In the latter case, Me is in fact a vacancy.¹⁶ In NiFe_2O_4 we again observe this set of ISCT transitions. In addition, we observe a strong, relatively broad transition at 2.9 eV. This transition is assigned to an IVCT transition between $[\text{Ni}^{2+}]$ and $[\text{Fe}^{3+}]$ ⁸ consistent with the observed absence of magneto-optical transitions in the equatorial Kerr spectrum of $(\text{Fe})[\text{NiCr}]\text{O}_4$ between 1 and 5.4 eV.¹⁷ Also, the strength and width of this transition is consistent with similar transitions in Fe_3O_4 . Furthermore, as follows from Fig. 2, the energy of an IVCT transition between two different cations is expected to be substantially higher than that between two identical cations, which in Fe_3O_4 occurs at 0.55 eV.

C. CoFe_2O_4

We have taken the complete dielectric tensors of CoFe_2O_4 and $\text{CoAl}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0.1, 0.6, 1$) from Martens *et al.*^{18,19} All four elements of the dielectric tensors of

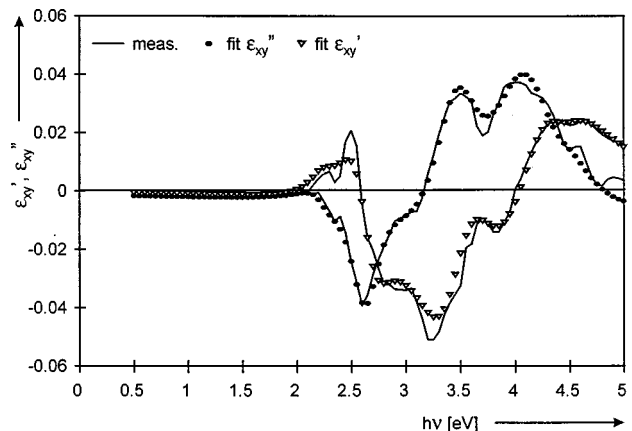


FIG. 5. The measurement and the fits of the real and imaginary part of the off-diagonal element of the dielectric tensor, ϵ'_{xy} and ϵ''_{xy} , of CoFe_2O_4 .

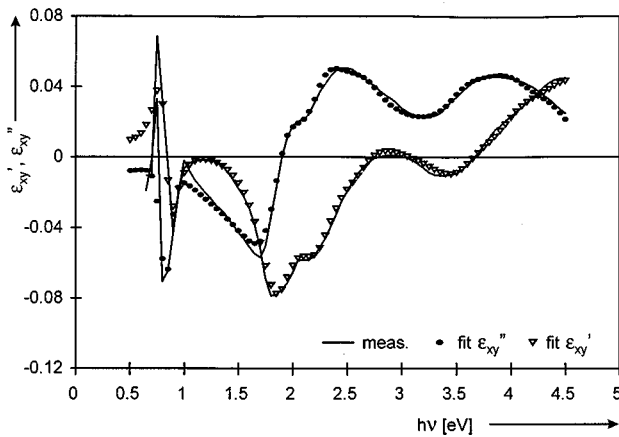


FIG. 6. The measurement and the fits of the real and imaginary part of the off-diagonal element of the dielectric tensor, ϵ'_{xy} and ϵ''_{xy} , of $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$.

CoFe_2O_4 and $\text{CoAl}_x\text{Fe}_{2-x}\text{O}_4$ were fitted simultaneously using a single set of parameters for all spectra, thus allowing trends in intensity upon Al^{3+} substitution to be detected. One must be aware that $\text{CoAl}_x\text{Fe}_{2-x}\text{O}_4$ changes from inverse to normal spinel between $x=0$ and $x=1.2$, i.e., Co^{2+} migrates to the tetrahedral site. In Fig. 6 the fit of the real and imaginary parts of the off-diagonal element of the dielectric tensor, ϵ'_{xy} and ϵ''_{xy} , of CoFe_2O_4 is presented. The transitions identified are given in Table I. The observed transitions above 2.5 eV are the same ISCT transitions observed in all spinel ferrites.⁸ Furthermore, at 2.21 eV an IVCT transition between $[\text{Co}^{2+}]$ and $[\text{Fe}^{3+}]$ is identified. As can be expected from Fig. 2, the energy of this IVCT transition between two different cations is substantially higher than that between two identical cations which in Fe_3O_4 occurs at 0.55 eV.³ The remaining two transitions are the only transitions which have still a significant intensity in CoAlFeO_4 ¹⁹ indicating that they are single-ion transitions, which we identify as CF transition of (Co^{2+}) . As shown in Table I, CoFe_2O_4 is the only spinel ferrite with a major contribution to the MO spectrum of CF transitions. The fact that we observe only two major CF transitions, and specifically in CoFe_2O_4 , is explained by the crystal field analysis given in Sec. II B. Note, that the width of the CF transitions (≈ 0.15 eV) is generally a factor two smaller than the width of the IVCT and ISCT transitions.

From the observed transition energies 0.83 eV and 1.82 eV one obtains for the Racah parameter, $B=0.08$ eV and for the crystal field splitting, $\Delta=0.48$ eV. The value of Δ is in line with expectations for oxides, but the value for B is significantly smaller than found in standard estimates from trends in divalent transition metal ions,²⁰ indicating strong hybridization between cobalt and oxygen. These values yield, using Eq. 3, a theoretical prediction for I equal to 0.41, while the observed intensity ratio is 0.25. The discrepancy is not serious and may partly be due to the difficulty of extracting accurate values for the linewidth from the experimental data. Qualitatively, the above simple crystal field description explains the fact that the lowest energy transition is the weakest of the two, and thus lends further support for our interpretation of these lines as Co^{2+} crystal field transitions.

D. General discussion

In Sec. II B we put forward theoretical considerations why in ferrites only ions in the high spin state on A sites are expected to exhibit CF transitions of considerable strength. The available literature confirms this. First, in the equatorial Kerr spectrum of $(\text{Fe})[\text{NiCr}]\text{O}_4$ between 1 and 5.4 eV no transitions whatsoever are found,¹⁷ ruling out the presence of CF transitions of $[\text{Ni}^{2+}]$ and (Fe^{3+}) . Second, in the dielectric tensor of $(\text{Fe}_{0.45}^{3+}\text{Co}_{0.55}^{2+})[\text{Fe}_{0.55}^{3+}\text{Co}_{0.45}^{2+}\text{Al}^{3+}]\text{O}_4$ only the two transitions assigned to CF transitions of (Co^{2+}) are prominent. The region between 2.5 and 4.5 eV is featureless although less than half of the $[\text{Fe}^{3+}]$ is replaced in this compound compared to CoFe_2O_4 . This makes the presence of CF transitions of $[\text{Fe}^{3+}]$ improbable.¹⁹ Third, minerals containing Fe^{2+} only are nearly colorless while simultaneous presence of Fe^{2+} and Fe^{3+} gives rise to intense absorption bands in the visible region.²¹ As a result, the presence of CF transitions of $[\text{Fe}^{2+}]$ in the visible range is improbable for Fe_3O_4 .

It has also been proposed that oxygen 2p to metal 3d charge transfer transitions contribute to the optical spectra of spinel ferrites. However, these transitions are expected to take place at energies well above 4 eV and to be more intense and broader than the transitions observed in the optical range. See, for instance, the transition near 6 eV in Fe_3O_4 .⁴

Most significantly, neither CF transitions, nor oxygen 2p to metal 3d charge transfer transitions explain why the intensities of certain transitions in the MO spectrum of Fe_3O_4 depend on both $[\text{Fe}^{2+}]$ and $[\text{Fe}^{3+}]$, while other transitions do not. By contrast, for IVCT transitions this is a preposition. In conclusion, the assignment to IVCT transitions of the major transitions in Fe_3O_4 explains the relative and absolute intensity, the relative and absolute energy, the width and line-shape, as well as, the dependence of these on various substitutions for all observed transitions and does so consistently for all spinel ferrites considered.

IV. WIDER SCOPE FOR IVCT TRANSITIONS?

We now discuss the possible relevance of IVCT transitions for other compounds than spinel ferrites. Since, the occurrence of IVCT transitions in mixed valence compounds

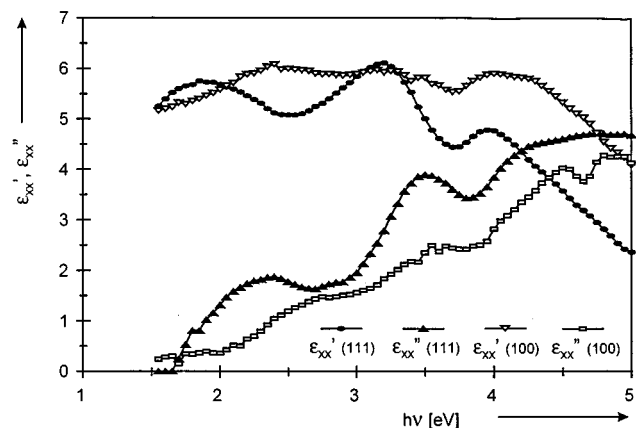


FIG. 7. Optical spectra of the (111) and (100) oriented CoO monolayers.

TABLE II. Transitions identified in (111) and (100) oriented CoO layers with thickness d_{CoO} .

Orientation	d_{CoO} (nm)						
(111)	162	ω	2.30	3.45	4.22	4.82	
		Γ	0.35	0.36	0.41	0.64	
		$(\epsilon_{xx})_{\text{max}}$	1.22	2.46	1.76	2.82	
(100)	94	ω	2.70	3.46	4.29	4.83	
		Γ	0.26	0.46	0.39	0.67	
		$(\epsilon_{xx})_{\text{max}}$	0.61	1.14	0.94	2.53	

is quite common,⁹ the spectrum of any compound which contains elements that can be present in two different oxidation states and which exhibits relatively broad and intense transitions in the optical range could be dominated by IVCT transitions. Possible candidates include Co_3O_4 ¹⁸ and manganites where the charge transport is believed to be due to $\text{Mn}^{3+}-\text{Mn}^{4+}$ polaron hopping similar to the $\text{Fe}^{2+}-\text{Fe}^{3+}$ hopping in Fe_3O_4 .²²⁻²⁴ Here we present experimental data indicating that this is actually the case for CoO. In Fig. 7 the real and imaginary part of the diagonal element of the dielectric tensor, ϵ'_{xx} and ϵ''_{xx} , respectively, i.e., the optical spectra, between 1.5 and 5 eV of (100) and (111) oriented CoO layers (94 and 162 nm thick, respectively) are presented. The energies of the identified transitions, are given in Table II. In the spectrum of the (100) oriented CoO the transition identified at 2.30 eV in the (111) oriented CoO appears to be missing, allowing the detection of a weaker transition at 2.70 eV. Thus far, only Pratt and Coelho have reported and assigned the transitions in the optical spectrum between 0.7 and 2.8 eV of (bulk) CoO in a study dating from 1959.²⁵ These authors observed transitions at 0.95, 1.61, 2.03, 2.05, 2.14, 2.30, 2.52, and 2.61 eV which they interpreted as CF transitions. However, no determination of the relative strength of these transitions was given. Direct inspection of the absorption spectrum presented by these authors, reveals a transition at 0.95 eV and a relatively strong transition around 2.3 eV and the tail of, in comparison, a much stronger transition above 2.8 eV, the edge of their measurement range. This is in agreement with our determination while our data extend to 5 eV. The assignment by Pratt and Coelho is in line with a recent theoretical study by de Graaf *et al.*²⁶

However, we note that the transitions in the 2.3–5 eV range are relatively broad ($\Gamma = 0.3-0.4$ eV) and intense compared to the transitions below 2.3 eV. Furthermore, the absence of the 2.3 eV transition in the (100) CoO layer is in line with the direction dependence of the absorption intensity of IVCT transitions which is predicted to be polarized along the metal–metal bond.¹⁰ This anisotropic behavior has also been reported for IVCT transitions in other compounds.⁹ Therefore, it is tempting to suggest that the major transitions in the 2.3–5 eV range are charge transfer type transitions.

V. CONCLUSIONS

The common feature of all spinel ferrites of the general type $\text{Me}_x\text{Fe}_{3-x}\text{O}_4$ with Fe^{3+} ions on both tetrahedral and octahedral sites is a set of ISCT transitions in the

magneto-optical spectrum: $(\text{Fe}^{3+})t_2 \rightarrow [\text{Fe}^{2+}]t_{2g}$ at 2.6 eV, $[\text{Fe}^{3+}]e_g \rightarrow (\text{Fe}^{2+})t_2$ at 3.5 eV, and $(\text{Fe}^{3+})t_2 \rightarrow [\text{Fe}^{2+}]e_g$ at 4.0 eV. This holds both for those spinel ferrites where Me is the nonmagnetic Mg^{2+} or Li^+ as well as for those where Me is the magnetic Fe^{2+} , Co^{2+} , or Ni^{2+} . For $\text{Me}=\text{Mg}^{2+}$, Li^+ or other nonmagnetic ions (or vacancies), this set of ISCT transitions is the main feature. In Fe_3O_4 also several IVCT transitions between $[\text{Fe}^{2+}]$ and Fe^{3+} contribute significantly: $[\text{Fe}^{2+}]t_{2g} \rightarrow [\text{Fe}^{2+}]t_{2g}$ at 0.56 eV, $[\text{Fe}^{2+}]t_{2g} \rightarrow [\text{Fe}^{2+}]e_g$ at 1.94 eV, $[\text{Fe}^{2+}]t_{2g} \rightarrow (\text{Fe}^{2+})e$ at 3.11 eV, and $[\text{Fe}^{2+}]t_{2g} \rightarrow (\text{Fe}^{2+})t_2$ at 3.93 eV. In NiFe_2O_4 an IVCT, $[\text{Ni}^{2+}] \rightarrow [\text{Fe}^{2+}]t_{2g}$ at 2.86 eV, is a main contributor. In CoFe_2O_4 CF transitions of tetrahedrally coordinated Co^{2+} , $(\text{Co}^{2+})^4A_2 \rightarrow ^4T_1(F)$ at 0.83 eV and $(\text{Co}^{2+})^4A_2 \rightarrow ^4T_1(P)$ at 1.82 eV, and an IVCT transition, $[\text{Co}^{2+}] \rightarrow [\text{Fe}^{2+}]t_{2g}$ at 2.21 eV, contribute significantly below 2.5 eV. There are indications for the presence of intervalence charge transfer transitions in other oxidic compounds such as CoO.

- J. Smit and H. P. J. Wijn, *Ferrites* (Philips Technical Library, Eindhoven, 1959).
- V. A. M. Brabers, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier Science, Amsterdam, 1995), Vol. 8, pp. 189–324.
- Z. Šimša, P. Široký, J. Koláček, and V. A. M. Brabers, *J. Magn. Mater.* **15–18**, 775 (1980).
- X. X. Zhang, J. Schoenes, W. Reim, and P. Wachter, *J. Phys. C* **16**, 6055 (1983).
- Š. Višňovský, V. Prosser, R. Krishnan, V. Pařízek, K. Nitsch, and L. Svobodová, *IEEE Trans. Magn.* **MAG-17**, 3205 (1981).
- H. Feil, Ph.D. thesis, University of Groningen, Groningen, The Netherlands, 1987; H. Feil *Solid State Commun.* **69**, 245 (1989).
- W. F. J. Fontijn, P. J. van der Zaag, M. A. C. Devillers, V. A. M. Brabers, and R. Metselaar, *Phys. Rev. B* **56**, 5432 (1997).
- W. F. J. Fontijn, P. J. van der Zaag, and R. Metselaar, *J. Appl. Phys.* **83**, 6765 (1998).
- G. C. Allen and N. S. Hush, "Intervalence-transfer absorption," in *Progress in Inorganic Chemistry*, edited by F. A. Cotton (Interscience, New York, 1967).
- D. M. Sherman, *Phys. Chem. Miner.* **14**, 355 (1987).
- G. B. Scott, D. E. Lacklison, H. I. Ralph, and J. L. Page, *Phys. Rev. B* **12**, 2562 (1975).
- J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, 1971).
- L. de Bont and V. A. M. Brabers (unpublished results).
- A. Petric, K. T. Jacob, and C. B. Alcock, *J. Am. Ceram. Soc.* **64**, 632 (1981).
- P. J. van der Zaag, W. F. J. Fontijn, P. Gaspard, R. M. Wolf, V. A. M. Brabers, R. J. M. van de Veerdonk, and P. A. A. van de Heijden, *J. Appl. Phys.* **79**, 5936 (1996).
- A. P. Khrebtov, A. A. Skochenskii, E. M. Speranskaya, and Kh. I. Turkmenov, *Izv. Akad. Nauk SSSR, Ser. Fiz.* **42**, 1652 (1978).
- G. S. Krinchik, K. M. Mukimov, Sh. M. Sharipov, A. P. Khrebtov, and E. M. Speranskaya, *Sov. Phys. JETP* **49**, 1074 (1979).
- J. W. D. Martens, W. L. Peeters, H. M. van Noort, and M. Erman, *J. Phys. Chem. Solids* **46**, 411 (1985).
- J. W. D. Martens, W. L. Peeters, P. Q. J. Nederpel, and M. Erman, *J. Appl. Phys.* **55**, 1100 (1984).
- J. Zaanen and G. A. Sawatzky, *J. Solid State Chem.* **88**, 8 (1990).
- G. McCarthy, *Am. J. Sci.* **12**, 17 (1926).
- C. Zener, *Phys. Rev.* **82**, 403 (1951).
- C. M. Varma, *Phys. Rev. B* **54**, 7328 (1996).
- T. Ishikawa, T. Kimura, T. Katsufuji, and Y. Tokura, *Phys. Rev. B* **57**, R8079 (1998).
- G. W. Pratt, Jr. and R. Coelho, *Phys. Rev.* **116**, 281 (1959).
- C. de Graaf, Ph.D. thesis, University of Groningen, The Netherlands, 1998; C. de Graaf, W. A. de Jong, R. Broer, and W. C. Nieuwpoort, *Chem. Phys.* **237**, 59 (1998).